Absorption detection at the quantum limit: Probing high-finesse cavities with modulation techniques

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I. Introduction

Two key ingredients are needed to achieve the highest sensitivity possible in the detection of atomic and molecular absorptions: enhancement of the absorption signal and elimination of technical noise. The absorption signal can be enhanced by using an optical cavity. However, care must be taken when measuring signals using an enhancement-cavity: the sharp resonances of the cavity can introduce additional noise through frequency-to-amplitude noise conversion. Technical noise, caused by such things as cavity vibration and drifts, can also prevent one from reaching the fundamental, quantum-noise limit. In this chapter we discuss the application of various modulation techniques and alternative experimental configurations that let one benefit from the signal enhancement aspect of a cavity while at the same time avoiding the introduction of additional noise in the detection process. As developers of sensitive absorption techniques, we would like to make these ideas and strategies available to the wider community, especially colleagues in other fields who have scientific problems that could be advanced if only a higher level of absorption sensitivity were available. We have a few such scientific problems and applications in mind ourselves and, most of this work has been motivated by two of these: an interest in the molecular vibration dynamics of weak transitions and the dream a general method to produce an accurate and precise series of frequency references throughout the visible and near-infrared wavelength regions. Molecular overtone transitions are suitable candidates for these studies because of the highly nonlinear characteristics of these vibrations and the generous spectral region over which they are found. With the development of the ultrasensitive absorption measurement techniques described in this chapter, such applications are headed towards fruition.

A. Signal enhancement of cavity

Improving sensitivity by placing a sample inside an optical resonator is a well-known technique and is most commonly explained in terms of the multipass effect. In fact, it was realized in the early days of laser development that a laser cavity is useful for absorption enhancement [1], because of the multipass effect and the delicate balance between the laser gain and intracavity absorption [2, 3]. However, in current implementations, it is often preferred to separate the absorber from the laser, in order to extend the experimental flexibility and to better characterize working parameters. For example, enhancement of absorption sensitivity has been accomplished by using long, multipass absorption cells [4]. Kastler suggested a Fábry-Pérot cavity could be used because its transmission is sensitive to small variations in absorption within the cavity [5]. Cerez *et al.* [6] first applied this external cavity technique to record high-resolution, saturated-absorption spectra. Ma and Hall [7] were able to use an external resonator combined with the optical heterodyne spectroscopy to achieve excellent signal-to-noise ratios. The use of an external cavity to detect molecular overtone transitions has also been demonstrated [8]. In linear-absorption experiments, enhancement cavities have been used most extensively in the context of ring-down spectroscopy [9, 10,11]. And finally, when the physical size of a cavity is brought down to a level such that the cavity mode volume is near the atomic "radiative" volume, a whole new set of quantum dynamics associated with the full quantum susceptibility can be explored within the setting of cavity quantum electrodynamics [12].

While we defer a detailed discussion of cavity enhancement effects to Section II, here we make a quick note of the advantages associated with an optical resonator. Of course, the well-known multipass effect leads to the enhancement of the effective absorption length by the factor of $(2 \times F/\pi)$, where F is the cavity finesse. Additionally, the cavity builds up the intracavity power, which allows for the study of nonlinear systems even with low-power laser sources. At the same time, however, the cavity reduces the output power level incident on the photodetector. Additionally, the geometrical self-cleaning and matching of the two counter-propagating waves inside the cavity are important both for eliminating pointing-direction related noise and for obtaining narrow, unshifted resonance lines [13]. Finally, a stable cavity can be used to stabilize a laser's frequency, by locking the laser to a cavity resonance, thereby reducing the detection noise.

B. Issues related to the technical and fundamental noise

Direct absorption measurements often suffer from intensity noise on the laser. The phenomenon of increasing noise amplitudes towards the low frequency region of the intensity spectrum has motivated development of modulation schemes, such as frequency-modulation spectroscopy, to encode and recover signals in frequency intervals with minimal technical noise. The use of an enhancement cavity, while effective in enhancing a signal, can also introduce some extra technical noise. For example, when the relative frequency fluctuation between the laser and the cavity resonance is of the same order as the cavity line width, frequency noise will be converted to amplitude noise in the detected signal, if a naïve, direct absorption approach is adopted. Because this noise conversion is inversely proportional to the cavity line width, the same enhancement factor that has improved the signal size can play an equal—but deleterious—role. Thus, while it is important to reduce noise amplitudes in the first place, it is usually equally imperative that some clever signal recovery techniques are employed to minimize the influence of the noise to the detection result.

For any absorption spectroscopy, the fundamental detection limit is reached when the minimum signal amplitude is fixed by the noise level associated with the discrete nature of the photon flux, which is a Poisson distribution for an ordinary laser output without technical noise. Such performance can be achieved when the technical noise is minimized by a differential measurement. For a true differential measurement to take place, quick comparisons of on-resonance and off-resonance information are required, that is, some sort of modulation technique should be employed. When combined with an effective modulation technique, the resonant cavity scheme approaches its potential: full signal enhancement without added noise. In the following sections, we will discuss two such experimental techniques.

C. Applications of sensitive detection

Sensitive, cavity-enhanced detection schemes have found many different applications, including the characterization of dielectric stacks [14]; measurement of ultraslow reflector velocities [15]; atmospheric sensing [16, 17]; detection of trace gaseous species [18]; absolute determination of absorption band strengths and species concentration [19]; analysis of combustion and plasma dynamics [20, 21]; study of chemical kinetics and molecular dynamics [22, 23]; tests of fundamental physical postulates [24-26]; improvements in laser stabilization and optical frequency metrology [27-29]; and research into quantum dynamics and quantum information [30-32]. Extension of these methods to study surfaces and condensed matter [33] and potential applications as medical instruments only make the field more exciting [34, 35].

1. II. Cavity enhancement: A simple physics picture

In this section we will discuss the basic physics associated with the cavity enhancement effect. We will derive some useful equations from different approaches and show that, like many other subjects, the cavity-enhancement principle finds manifestation in different forms. It is useful to explore these different aspects as each highlights different practical consequences and can lead to effective experimental techniques.

A. Enhanced radiation (absorption) of molecular dipole moments inside a cavity

Perhaps cavity enhancement can be most simply understood from the cartoon picture shown in Fig. 1 (a). Suppose a single atom is present within the mode volume of a resonant light field of cross section *a* and length *d*. Denoting the atomic dipole moment μ and the transition wavelength λ (angular frequency $\omega = 2\pi\, c/\lambda$, with *c* being the speed of light), we have the atomic decay rate $\gamma \propto \mu^2 / \lambda^3$ and the atom-field coupling (Rabi) frequency $g \propto \mu \cdot \sqrt{\omega/(a \cdot d)}$. In this last formula, we have substituted the electric field generated by a single (QED vacuum) photon. The absorption coefficient (α) can be interpreted as arising from the atomic transition rate determined from the Fermi golden rule, g^2/γ, multiplied by the interaction time, *d/c*. Therefore $\alpha \propto \left(g^2/\gamma\right) \cdot d/c \approx \lambda^2/a \approx \sigma_0/a$, with σ_0 being the resonant absorption cross section of the atom. From this intuitive picture, we can immediately understand that if a cavity is placed around the atom with the intracavity photon lifetime resonantly increased to $\tau_{cavity} = (2F/\pi) \cdot d/c$, the absorption coefficient becomes $\alpha_{enhanced} = \left(g^2/\gamma\right) \cdot \tau_{cavity} = (2F/\pi)\alpha$.

B. Derivation of the length enhancement factor and other relevant cavity properties

We can also start our discussion of cavity-enhancement by looking into the cavity properties. The basic understanding is developed by placing the absorbing atoms or molecules in an optical cavity and then comparing the absorption level to the intrinsic loss of the cavity. Thus low-loss mirrors (and consequently high-finesse cavities) help to enhance the signal contrast. Figure 1 (b) shows a standing-wave optical resonator. The two mirrors are assumed to be identical, with power transmission of *T* and loss of *A*. The total empty cavity loss is $L_{cav} = 2(T + A)$. We denote the optical input power as P_{in}, the cavity-reflected power as P_r, and the cavity-transmitted power as P_t. The cavity finesse (*F*) is

$$F = \frac{2\pi}{L_{cav}} = \frac{\pi}{T+A}\ . \tag{1}$$

The resonant cavity reflection efficiency, transmission efficiency, and intracavity build-up power, P_c, can be expressed, respectively, as

$$\frac{P_r}{P_{in}} = \left(\frac{A}{T+A}\right)^2,$$
$$\frac{P_t}{P_{in}} = \left(\frac{T}{T+A}\right)^2, \quad and \tag{2}$$
$$\frac{P_c}{P_{in}} = T\left(\frac{1}{T+A}\right)^2.$$

Consider a cavity of length d, filled with a weakly-absorbing gas sample with an absorption coefficient of α per unit length. (By weakly-absorbing we mean the cavity round trip fractional power loss can be written as $1-\exp(-2\alpha d)\approx 2\alpha d$.) In a direct absorption measurement with a sample cell of length d, the output power is; $P_{out} = P_{in}\cdot e^{-\alpha d} \sim P_{in}(1 - \alpha d)$. Therefore, the absorption signal is $(P_{in}\cdot \alpha d)$. When the sample is placed inside a cavity, the transmitted power is modified according to Eq. (2)

$$\frac{P_t}{P_{in}} = \left(\frac{T}{T+A+\alpha d}\right)^2 \approx \left(\frac{T}{T+A}\right)^2\left(1-2\frac{\alpha d}{T+A}\right). \tag{3}$$

The detected signal contrast in the cavity transmission is therefore enhanced,

$$\frac{\delta P_t}{P_t} = -2\frac{\alpha d}{T+A} = -\frac{2F}{\pi}\cdot(\alpha d)\,. \tag{4}$$

In practice, the mirror parameters can be selected to maximize the resonant cavity transmission, by taking into consideration intracavity gas absorption. This can be especially advantageous if the anticipated sample absorption is of the same order or larger than the mirror transmission coefficients. It is also worth noting that, although the cavity finesse is determined by the sum of the mirror transmission T and loss A and neither quantity appears explicitly in Eq. (4), it is optimal for T to be dominant over A, because this increases the absolute size of the absorption signal [Cf. Eq. (3)].

C. Constructive interference of atomic/molecular radiation

It is clear from Eq. (2) that the intracavity circulating power can be much larger than the input power. This power buildup is essential to have an appreciable level of saturation for very weak transitions, which enables resolution of sub-Doppler resonances. The strong light field drives phase-coherently the atomic or molecular dipole moments. The radiation from these prepared dipole moments is the signal to be detected. However, the strong background of the unabsorbed incoming light sets the detection noise level, the shot-noise level in the ideal case (Cf. Section III). With the build-up cavity approach, this potentially large noise contribution from the intracavity field is reduced after the sample has been prepared and before the final detection. When the cavity is tuned onto a molecular line, the major part (determined by the cavity efficiency) of the molecular signal will leak out of the cavity to reach a detector, while a similar, or smaller, portion of the input power will be transmitted by the cavity and reach the same detector to set the shot-noise limit. The large intracavity buildup power, however, will remain trapped inside, after having prepared the phase-coherent molecular dipole moments of an enhanced magnitude. This result, although explained here from yet another perspective, is the same cavity enhancement effect discussed in the previous paragraphs.

To mathematically clarify the above discussion, we note that the intracavity field E_c is related to the input field E_{in} by $E_c = E_{in} \cdot \sqrt{T}/(T + A)$ [Cf. Fig. 1(b)]. The radiation field of the prepared dipole moments can be written as $E_{atom} = -E_c \cdot (\alpha d/2)$, where the minus sign accounts for the negative interference between the sample radiation and the original field that leads to absorption. The integrated intracavity (single-pass) absorption signal is (αd) and the factor of ½ reflects the fact that we are now dealing with the field amplitude. When the cavity is tuned to the atomic resonance, this atomic signal will be resonantly enhanced by constructive interference, by a factor of 2/(T+A). Here the factor of 2 accounts for the bi-directional effect in the cavity. Finally the field will leaking out of the cavity is attenuated by $\sqrt{T}$ before reaching final photodetector. The final field can thus be expressed as

$$E_{atom-final} = -\sqrt{T} \cdot E_c \left(\frac{\alpha d}{2}\right) \cdot \left(\frac{2}{T + A}\right) = -\frac{T}{T + A} E_{in} \cdot \left(\frac{\alpha d}{2}\right) \cdot \left(\frac{2F}{\pi}\right). \qquad (5)$$

When this quantity is compared to the transmitted local oscillator field, $E_{in} \cdot T/(T + A)$, and the enhancement factor is again ($2F/\pi$).

From a practical point-of-view, using a cavity is also attractive when the laser source has a relatively large amplitude noise. To achieve shot-noise limited detection in this case, the optimum intensity range tends to be pushed to a lower value. But when a buildup cavity is used, the detector does not have to receive the large intensity. Thus, one can take advantage of the large intracavity fields, while still having a transmitted power that allows one to operate in the shot-noise limited regime. This effect is similar to the result of polarization spectroscopy [36] or interference filtering.

D. Influence of the cavity physical size

Although our discussion has focused mainly on the semiclassical aspect of the light-matter interaction, it is nonetheless interesting to make a quick note on the connection between this classical picture of cavity-enhanced spectroscopy and optical cavity based quantum electrodynamics (QED). When the cavity volume is chosen to be not far away from the critical radiation volume of the atom, namely $V_{critical} = \lambda^2 \cdot c/\gamma$, the atom-cavity interaction will have to be treated in a full quantum picture, considering that the interaction strength g can be larger than either the atomic decay rate γ or the cavity decay rate κ. In the optical bistability and cavity QED literature [37, 38], there is an atomic co-operativity parameter defined as $N g^2/\kappa\gamma$, where N is the number of atoms. This quantity signifies the level of modification of the empty cavity properties by the presence of atoms. Calculation reveals that the co-operativity parameter is nothing but the now familiar $(2F/\pi)\alpha d$.

III. Signal encoding and extracting: modulation-plus-heterodyne detection

Parallel with signal enhancement, the issues of detection noise and how to reach the fundamental noise limit are equally critical to the implementation of sensitive spectroscopy. In this section, we will concentrate on the noise aspect of signal extraction.

The ultimate detection sensitivity is achieved when we are able to observe each absorption event individually, and when the noise is limited by the uncertainty of an event occurrence. This is referred to as the shot-noise limit. From this we understand that the shot-noise is associated with the discrete nature of the interaction between matter and the photon stream. The shot-noise is fundamental in that it reflects the quantum nature of light from ordinary thermal sources and lasers far above threshold, sources that carry Poissonian statistics. Radiation fields can also be "squeezed" to have sub-Poissonian levels of fluctuation, providing an anomalously low fluctuation level for the photocurrent (*i.e.* subshot-noise). Here our task is just to be able to approach the standard, shot-noise level of absorption spectroscopy.

A. Fundamental limits versus technical noise

As noted in Section II, the physical origin of the absorption process can be understood as the destructive interference between the incident radiation and the electric field generated by the coherently driven dipole moments of the sample. Therefore, direct absorption can be viewed as a homodyne detection between the two interfering fields that have the same frequency. Maximum sensitivity occurs when the probe field has no amplitude noise beyond its intrinsic quantum fluctuations. Given a detection bandwidth of B and the average photocurrent i_{dc}, the associated shot-noise current is given by $i_n = \sqrt{2ei_{dc}B}$, where e is the electron charge. Taking the photodetector responsivity as η (dimensions of electrical current per unit power incident on the detector) and P_0 as the incident radiation power, then $i_{dc} = \eta P_0$ and the absorption signal $i_{sig} = (\alpha d)\eta P_0$. The shot-noise will set the fundamental sensitivity limit for straight absorption spectroscopy. When the signal-to-noise (*S/N*) ratio is one, *i.e.* when the molecular absorption is equivalent to the shot noise in the measurement bandwidth, we obtain the minimum detectable absorption as

$$(\alpha d)_{\min} = \sqrt{\frac{2eB}{\eta P_0}} \quad (6)$$

This direct absorption sensitivity can detect an integrated absorption of 2×10^{-8} for a 1 s averaging time for P_0 = 1 mW and a reasonable η (≈0.8 A/W).

Needless to say, this number seems optimistic when compared to experience. In practice, noise of various technical origins tends to become dominant in the low frequency ranges, and actual laser systems display vastly more noise than the shot-noise limit. This extra technical noise may originate in inadequately smoothed power-supply potentials, laboratory vibrations that randomly dither the laser's alignment and mode structure, electromagnetic pickup from high-frequency or high-current devices, or unwanted optical feedbacks. A noisy background severely impacts the measurement of small signal changes, and typically the resultant *S/N* is several orders of magnitude worse than the shot-noise limit. In order to avoid excessive low-frequency noise of technical origins, one can use modulation techniques, either on the laser amplitude or frequency, to encode and then detect the absorption at a higher frequency and within a narrower bandwidth. Of course amplitude modulation of the laser will result in enhanced *S/N* only if the signal response is nonlinear. Otherwise one just has a high *S/N* way to see that the laser's power is unsteady. Reduced-background detection techniques (such as polarization and interference spectroscopy) are also quite often used in avoiding excessive noises.

B. Introduction to optical heterodyne detection

Before we get into the details of modulation techniques, it will be useful to become familiar with the approach of optical heterodyne detection. The reason is that modulation detection can often be understood as a heterodyne interaction between one optical field (the carrier) and another (a modulation sideband). The optical power will generally have a time-dependent term if the applied laser field is the sum from two sources, *i.e.* $[E_1(t)+E_2(t)]^2$. For simplicity we have neglected important interference details by assuming the two contributing fields to be mutually mode-matched. With $E_1(t)=E_1\cos(\omega_1 t)$ and similarly for E_2 and ω_2, when the difference of the two applied frequencies is within the detector's response bandwidth, we expect a detected photocurrent of the form $i(t)=\left(i_1+2\sqrt{i_1 i_2}\sin(\omega_1-\omega_2)t+i_2\right)$. We refer to the cross term at the difference frequency as the heterodyne response. If we had chosen to think of the field E_2 as somehow different, if for example it were a weak field being produced by a molecular sample, one can see one of the advantages of the heterodyne approach: the scale of the beat current can be increased by increasing the size of E_1, which is referred to as the "local oscillator" (LO) field, following the convention of radio-frequency engineers. It is important that the *S/N* is not degraded by use of a larger LO power. Some technical remarks below return to this subject.

Any real photodetector will have some output noise, even in total darkness. If we attempt direct detection of a weak signal, the incident power will need to be sufficient to overcome the detector's intrinsic noise. Consider the heterodyne case: now the signal-bearing light power is represented by the cross-term between the local oscillator field and the weak signal field, *i.e.* $i_{sig} \propto E_1 E_2$. On the other hand, because $E_1 >> E_2$, the shot-noise of the total photocurrent will be dominated by the LO power, *i.e.* $i_n \propto \sqrt{E_1^2} = E_1$. It is only this noise term that needs to be adequately large to mask the detector noise. So by merely using a stronger LO field, we can overcome the appreciable noise produced by the amplifier circuit that converts the photo current into an output voltage. Ideally then, the *S/N* of the heterodyne detection depends only on the amplitude of the signal beam (E_2) and the LO amplitude is cancelled out in the final *S/N* ratio (see Fig. 2).

Of course, this LO power can carry laser intensity noise to the detector as well. Any non-fundamental noise imposed on this intensity will be directly converted into unwelcomed noise. But typically this noise, called "technical noise" to identify its origin, is concentrated at lower frequencies and arises from "1/f" noise processes. Technical noise seldom has a pure spectrum, and typically has spectral density that is concentrated at power-line harmonics and low frequencies associated with laboratory vibrations. Various noise processes in semiconductor devices are also restricted to audio frequencies and below. So an important idea toward achieving low-noise performance is to place the information-carrying heterodyne signal at a frequency sufficiently high that a negligible level of technical noise is carried by the LO field. This is the usual motivation for using some form of modulation-based signal recovery approach.

C. Motivation and Concept of modulation

From a time-domain point-of-view, signal detection schemes employing modulation (ac) methods permit comparison of two cases in quick succession. With suitable modulation schemes, these states can represent the on-resonant and off-resonant cases, being sampled in rapid succession. By simultaneously obtaining and subtracting these, one provides a signal channel with no output unless there is a resonance. The modulation approach therefore allows efficient extraction of weak signals from a noisy background. Lorentzian signal recovery with modulation methods has been well documented [39, 40]. The lock-in detection can provide the first-, second-, and third-derivative type of output signals. In this type of modulation spectroscopy, the modulation frequency is often chosen to be relatively low to avoid distortions of the spectral profile by the auxiliary resonances associated with modulation-induced spectral sidebands. However, this choice of low-frequency operation usually limits the achievable signal-to-noise ratio, because of the excess noise of the laser source at low frequencies. To recover the optimum signal size, large (comparable to the absorption resonance width) modulation amplitudes can be employed. In this case, however, the intrinsic line shape is masked by this signal acquisition process.

Using high modulation frequencies, frequency-modulation (FM) spectroscopy has become one of the most powerful techniques available for sensitive and high-speed detection of weak absorption signals [41-43]. In principle, FM spectroscopy using a high modulation frequency located in a spectral region where the amplitude noise of the laser source approaches the shot-noise offers a detection sensitivity close to that of Eq. (6). A reasonable modulation index is still needed to recover an adequate signal. However, the associated line width broadenings and line shape distortions associated with low-frequency modulation processes are not present in high-frequency FM spectroscopy. Instead, one obtains added spectral features. Thus, the modulation frequency should be large compared to the width of the spectral feature under study. When scanning through an absorption resonance, each component of the FM spectrum, which consists of a central carrier and weaker sidebands, interacts with a spectral feature, thereby preserving the resolution of the laser. The high bandwidth, or equivalently speaking, a high Nyquist sampling frequency, associated with the high-frequency modulation enables rapid signal recovery.

When received by a square-law photodiode, a pure frequency modulated spectrum will display no photocurrent at the modulation frequency. This is because the two beat signals between the carrier and either sideband are equal in magnitude but opposite in phase. Hence the net result is a perfect cancellation. However, the presence of an absorption feature is revealed as an attenuation and phase shift of one or several of the optical frequency FM components. The perfect FM balance is therefore upset, and the resultant optical signal has an amplitude-modulated component. The photocurrent signal can then be phase-sensitively detected using standard radio frequency techniques, yielding an absorption or dispersion line shape, depending upon the detection phase. The redistribution by deliberate FM modulation of some of the carrier power into FM sidebands causes only a slight penalty in the recovered signal size. When the modulation index β is on the order of unity or less, the FM spectrum can be approximated by a carrier [$\approx J_0(\beta)$] and two first order sidebands [$\approx J_1(\beta)$]. (Here J_i is the i-th order Bessel function.) If only the carrier is tuned to interact with a narrow sub-Doppler resonance, then the detection process is intrinsically dispersion-sensitive. Assuming the total probe power is still P_0, the detected shot noise current is given by $\sqrt{2eB\eta P_0\left(J_0^2 + 2J_1^2\right)} \approx \sqrt{2eB\eta P_0}$. The signal current arising from the heterodyne beat between the carrier and the sidebands becomes $\sqrt{2}\eta P_0 J_0 J_1 \cdot \phi$, with ϕ being the associated resonance phase shift. The magnitude relationship between dispersion and absorption ($\phi = \Delta n \cdot \omega d/c$ and $\Delta n = \alpha \cdot \lambda/4\pi$, where Δn is the resonance-inflicted change of refractive index) sets the scale of the equivalent minimum absorption at the shot-noise limit:

$$(\alpha d)_{\min} = \sqrt{\frac{2eB}{\eta P_0}} \frac{\sqrt{2}}{J_0(\beta) J_1(\beta)} \,. \tag{7}$$

The modulation-dependent function $J_0(\beta)$ $J_1(\beta)$ has its maximum value of 0.34 at $\beta \approx 1.1$. Compared to Eq. (6) for the ideal case of homodyne detection, FM heterodyne detection suffers a factor of about four loss in sensitivity for fixed total optical power. This is a small price to pay for completely avoiding the laser's technical noise. The *S/N* loss arises in part because of the power reduction resulting from convertion of some of the main carrier to sidebands and in part from the down-conversion of shot-noise from two additional spectral windows by the two sidebands. Carefully executed FM detection can often nearly reach the sensitivity limit set in Eq. (7).

D. Combining cavity enhancement with modulation: Introduction to the techniques of ac chop ring-down and cavity-enhanced FM spectroscopy

In the Sections IV and V, we will describe two techniques that combine the cavity enhancement approach with modulation techniques to reach the shot-noise limit. These techniques improve the detection sensitivity by a factor of ($2F/\pi$), without the added noise factors that can be associated with the use of an enhancement cavity. The two approaches are seemingly quite different, with the first one best understood from the time-domain picture in the context of cavity field ring-down, while the second one is more related to the frequency modulation spectroscopy discussed above. In the chop ring-down spectroscopy [44], two slightly different ring-down time constants are compared, one associated with an empty cavity and the other with additional intracavity loss. Typically the comparison rate is in the audio frequency range. The technique is suitable for linear absorption measurements. In the cavity-enhanced FM spectroscopy [45], the on-resonance and off-resonance information is compared at a radio frequency rate. This technique can be applied to both linear and nonlinear (sub-Doppler resolution) spectroscopy. The two techniques employ quite different experimental setups, but both achieve near shot-noise limited absorption sensitivity. As will be evident below, the two approaches are intimately related, through the common features of cavity enhancement and shot-noise limited signal recovery, and therefore the sensitivity can be calculated using (nearly) the same formula.

IV. Weak absorption measured by field decay (time-domain)

This section discusses a cavity-enhanced methods for measuring very weak absorptions. In these measurements, two cavity modes, one probing the empty cavity and the other probing intracavity absorption, are present simultaneously but the intensities are temporally out of phase, with one mode decaying and the other rising, when viewed in cavity transmission. Heterodyne detection between the two modes reveals the dynamic time constants associated with the empty cavity and the intracavity gas absorption. Quick, differential measurement eliminates a great deal of technical noise. This is essentially an improved version of the cavity ring-down technique [10] and it yields a 1×10^{-10} absorption sensitivity using microwatt-level laser powers.

A. Brief introduction to cavity ring-down spectroscopy

Inside a high-finesse cavity, light completes many round-trips, and this effectively increases the path length by ($2F/\pi$). Cavity ring-down spectroscopy (CRDS) exploits this cavity-enhancement property by measuring the decay of the intracavity field during these many round-trips. Because the decay rate increases when an absorber is inside the cavity, this method can be used as a spectroscopic tool. For example, an unknown absorption coefficient is determined by comparing the cavity losses when the absorber is in the cavity to the known mirror losses. Ideally, the mirror losses should be of the same order of magnitude of the absorption level to be measured, because this makes the "background" comparable to the "signal," and increases the measurement sensitivity. Because CRDS measures the decay dynamics after the field has built-up inside the cavity, it largely eliminates the technical noise on the radiation field.

However, as commonly implemented, CRDS has two shortcomings. The first is that CRDS, in its ordinary form, is a long time-interval measurement. Two decay-time measurements are made, one on the empty cavity decay and the other on cavity-plus-sample. The difference between the two measured decay rates contains the desired information. However, the time between the two measurements allows slow drifts and other technical noise to contaminate the data. The second problem is that technical noise, rather than shot-noise, dominates the tail-end of a ring-down signal. That is, technical noise is the dominant noise source in the signal beyond the point where the field's shot-noise equals the instrument's technical noise. To overcome this limitation, a heterodyne technique was developed [11] that superimposes a large local oscillator field onto the decay field so that the resultant beat signal can always be shot-noise limited. However some form of modulation strategy is still needed to achieve a rapid differential measurement.

With a modulation technique to compare the signal against the background at short time intervals, one can accurately subtract noise in the background from the useful signal. In the context of CRDS, two decay constants are to be compared, one associated with the empty cavity loss (off-resonance for the intracavity gas sample) and the other one associated with the total intracavity loss, in a quick succession. This concept can be realized if two different optical frequencies are fed into two cavity modes, one mode centered on the molecular transition and the other one far detuned from it. With the aid of cavity filtering and an intensity-stabilized laser, it is possible to reach the fundamental, quantum-noise limit to within a factor of four using this approach [44].

B. Concept of AC chop ring-down – Separating the ring-down fields associated with cavity and molecules.

Figure 3 illustrates the basic scheme of the AC chopped ring-down method. An intensity-stabilized, continuous-wave (cw) laser beam is split by two acousto-optic modulators (AOMs) into two beams with an impressed 1.3 GHz frequency offset, i.e., $\Omega_1 - (-\Omega_2) = 1.3\,GHz$. This offset is chosen so that both beams can resonate with the cavity simultaneously (four mode orders apart, cavity free-spectral-range (*FSR*) splitting frequency 318.34 MHz, finesse $F \approx 90{,}000$). After being combined and mode-coupled into the cavity, the two beams give 3 μW in each cavity transmission. However, the intensities are chopped out-of-phase by the AOMs, such that only one beam is input at a time. Despite the switching, a detector viewing in cavity reflection is able to maintain the laser/cavity lock using the Pound-Drever-Hall technique [46], with the radio-frequency (rf) sideband generated by the electro-optic modulator (EOM). Inside the cavity there is one decaying mode and one rising mode. That is, on the time scale of a ring-down time constant, the cavity mode that is being coupled in will rise exponentially while the other mode, with its input switched off, will decay exponentially. In transmission, the heterodyne beat waveform between the two modes is detected. Demodulation against the known carrier frequency (1.3 GHz) then yields the heterodyne beat amplitude, which contains the information of dynamic variation of both modes. In the case of empty cavity, the beat amplitude waveform remains unchanged at neighboring chopping cycles. However, when a mode is tuned to a molecular resonance, the system exhibits two slightly different time constants. The beat waveform becomes asymmetric between the adjacent cycles, and the difference is related to the intracavity absorption. The period of chopping cycle can be chosen to roughly match the field decay time (1/*e*) of the empty cavity. This technique thus offers a quick comparison of on-resonance and off-resonance information and substantially suppresses technical noise. Because each ring-down waveform is measured during a chopping period that is on the order of the 1/*e* field decay time, shot-noise dominates throughout the signal acquisition.

To expand the foregoing discussion, consider the following theoretical model for this technique. Suppose the round-trip loss of the empty cavity is L_{cav}, the round-trip absorption of the intracavity medium is $2\alpha d$, and the round-trip time of light within the cavity is $t_{round-trip}$. For a cavity mode that is far detuned from the medium resonance, the characteristic time constant associated with the mode dynamics is given by

$$\tau_{cav} = \frac{2t_{round-trip}}{L_{cav}} . \qquad (8)$$

We note that this is the 1/*e* decay time of the field, a relevant quantity because we deal with heterodyne detection between two fields. For the mode that is tuned to the absorption, the decay time constant becomes

$$\tau_{abs} = \frac{2t_{round-trip}}{L_{cav} + 2\alpha d} . \qquad (9)$$

Following the intensity-chopping scheme of Fig. 3, let us assume that during the period of [0, $\Delta t/2$], mode 1 (E_1) of empty cavity is switched on, while mode 2 (E_2), which sees the additional intracavity absorption, is switched off. After some cycles, the two field amplitudes evolve as,

$$E_1 = c_1\left[1+\exp\left(-\Delta t \big/ 2\tau_{cav}\right) - \exp\left(-\, t \big/ \tau_{cav}\right)\right];$$

$$E_2 = c_2 \exp\left(-\, t \big/ \tau_{abs}\right). \qquad (10)$$

Here c_1 and c_2 are amplitude coefficients for E_1 and E_2, respectively. In the next half cycle, [$\Delta t/2$, Δt], we reverse the two fields such that mode 1 is switched off and mode 2 on. The product of the two field amplitudes is what we detect in the demodulated signal of the cavity transmitted heterodyne beat. If we compare the signal of the two neighboring half-cycles, we obtain the information of absorption in the following form,

$$\left(E_1E_2\right)_{[0,\Delta t/2]} - \left(E_1E_2\right)_{[\Delta t/2,\Delta t]} = c_1c_2\left[\left(1+e^{-\frac{\Delta t}{2\tau_{cav}}}\right)e^{-\frac{t}{\tau_{abs}}} - \left(1+e^{-\frac{\Delta t}{2\tau_{abs}}}\right)e^{-\frac{t}{\tau_{cav}}}\right].$$

(11)

Figure 4 shows the results obtained from Eqs. (10) and (11). The chopping period, Δt, is chosen to be $4\,\tau_{cav}$, and the time axes have been normalized to τ_{cav}. In the case of an empty cavity, shown in the right column, the switched waveforms of mode 1 and mode 2 are totally symmetric, resulting in an equivalent signal of the beat amplitude during adjacent half-cycles and thus the difference gives a zero baseline. When mode 1 and mode 2 see different intracavity loss, as shown in the left column of the figure, there is a clear asymmetry in the heterodyne beat amplitudes between the adjacent half-cycles. The differences, as plotted in the bottom curve, show the level of additional absorption. In this case, the medium absorption is 10% of the empty cavity losses.

The fundamental limit of the obtainable sensitivity of this method follows from Eqs. (10) and (11). Suppose the two modes have the same amplitude coefficients, $c_1 = c_2 = \sqrt{P_0}$, in transmission, and the light is converted to a photocurrent, according to $i = \eta \times P$, where η is as before the detector responsivity. The demodulated beat current is $\eta \times 2E_1E_2/\sqrt{2}$. For simplicity of presentation, we use the small absorption limit, $\tau_{cav} \approx \tau_{abs}$, and assume $\Delta t/\tau_{cav} \geq 10$. The difference signal of Eq. (11) becomes

$$i_{signal} \approx \eta \frac{2}{\sqrt{2}} P_0 \left[e^{-\frac{t}{\tau_{abs}}} - e^{-\frac{t}{\tau_{cav}}} \right] = -\eta\sqrt{2}P_0 e^{-\frac{t}{\tau_{cav}}} \left[1 - e^{-t\left(\frac{1}{\tau_{abs}} - \frac{1}{\tau_{cav}}\right)} \right] \qquad (12)$$

$$= -\eta\sqrt{2}P_0 \left(\frac{1}{\tau_{abs}} - \frac{1}{\tau_{cav}} \right) \times t \times e^{-\frac{t}{\tau_{cav}}} \quad .$$

Because the beat amplitude reaches the maximum when $E_1 = E_2$, we have $\exp(-t/\tau_{cav}) \approx 1/2$, and $t = \tau_{cav} \ln 2$. With the help of Eqs. (8) and (9), we obtain

$$i_{signal} = -\eta\sqrt{2}P_0\tau_{cav} \frac{\ln 2}{2} \frac{2\alpha d}{2t_{roundtrip}} = -\eta P_0 \frac{\ln 2}{\sqrt{2}} \frac{2\alpha d}{L_{cav}} . \qquad (13)$$

The shot-noise produced by the photocurrent, $i_{DC} = \eta \cdot 2\left(\frac{\sqrt{P_0}}{2}\right)^2 = \eta P_0/2$, is $i_{noise} = \sqrt{2eB \times \eta P_0/2}$. The resultant *S/N* is

$$\left| \frac{i_{signal}}{i_{noise}} \right|_{\substack{shot\\noise}} = \sqrt{\frac{\eta P_0}{eB}} \frac{\ln 2}{\sqrt{2}} \frac{2\alpha d}{L_{cav}} . \qquad (14)$$

In terms of the noise-equivalent sensitivity of single pass integrated absorption, we set *S/N* =1, and

$$(\alpha d)_{\min} = \frac{1}{\ln 2} \sqrt{\frac{2eB}{\eta P_0}} \frac{L_{cav}}{2} = \frac{2}{\ln 2} \sqrt{\frac{2eB}{\eta P_0}} \frac{\pi}{2F} \quad . \qquad (15)$$

Compared to Eq. (6), we see that except for a numerical factor of about three, the shot-noise limited ac chop ring-down spectroscopy provides an enhanced detection sensitivity by a factor of $(2F/\pi)$ over the fundamental limit of direct absorption measurement.

C. Experimental results of AC chop ring-down spectroscopy

The concept discussed in the preceding section has been demonstrated in the measurement of rovibrational transitions of acetylene. The experiment used a Yb:YAGlaser. The transition involved was the $3\nu_3$ R(29) overtone of C_2H_2 , located at 1031.6528 nm, with an absorption coefficient of 4×10^{-6} $(\text{Torr}\cdot\text{cm})^{-1}$. In the 46.9 cm long cavity, a gas pressure of a few milliTorr (1 Torr = 133 Pa) was typically used, giving 1×10^{-6} level of absorption. The beam chopping frequency was 1.4 kHz, corresponding to $\Delta t = 714\,\mu s$. The cavity transmission was received by an avalanche photodiode (APD), and the beat signal was sent to an rf spectrum analyzer for demodulation. The frequency reference of the rf spectrum analyzer was tied to the rf signals used to drive the AOMs. In the linear amplitude display mode, the video output of the spectrum analyzer in zero-span-mode provides a phase-insensitive demodulation for the heterodyne beat. To measure the empty cavity finesse, both mode 1 and mode 2 were tuned out of the molecular resonance. Fig. 5 shows a representative trace of the demodulated heterodyne beat ring-down waveform with an overlaid theoretical fit. As can be seen, the model presented above produces an excellent fit, giving the empty cavity field ring-down (1/*e*) time of 90 µs. This leads to a cavity line width (full-width at half-maximum) of 3.5 kHz and a finesse of 90,000. Within the detection bandwidth of 173 kHz, the recovered *S/N* was150, about half the expected value. This wass partly attributable to "ringing" of the spectrum analyzer's rf filter function, which is optimized for the frequency domain analysis. It was not possible to use a smaller bandwidth on the instrument without distorting the signal.

Mode 2 is then tuned to the center of the acetylene resonance, and the ring-down waveform becomes clearly asymmetric in the neighboring half cycles. Figure 6 shows a set of experimental data where intracavity gas pressure was varied to generate four different intracavity absorption levels (expressed in terms of single-pass in the graph). The respective ring-down beat waveforms are shown in the left column of the figure. The absorption data (shown in the right column) were produced in the following way. First, a copy of the original data was shifted by a half chopping cycle along the time axis. The differences between the original data and the shifted data gave the absorption signals. With a single pass absorption of 1.7×10^{-6}, the acquired S/N was 10 with a bandwidth of 173 kHz. The absorption sensitivity normalized to 1 s averaging time was then 1.6×10^{-10}. In steady state (no chopping), each mode has 3 µW (P_0) in the cavity transmission. Given an η for the APD of 0.3 A/W, the shot-noise limited sensitivity should have been $\approx1.2\times10^{-11}$ at 1 s averaging. However, because the APD has an excess noise factor of about three, the expected minimum absorption sensitivity was $\approx4\times10^{-11}$, which is within a factor of four of the experimental result.

One can notice in Fig. 6 that the recovered signal amplitude does not increase linearly with respect to the additional intracavity absorption. Of course one expects that if the gas absorption greatly exceeds the level of the empty cavity loss, signal saturation will occur. In Fig. 7(a), the signal contrast is shown against the intracavity absorption normalized to the empty cavity loss. The dotted curve is calculated assuming that the coupling power to mode 2 (the absorbing mode) remains a constant. However, we know that with added loss inside, the power coupling efficiency to the cavity changes, and the available power for mode 2 will decrease. Therefore for a fixed incident power, the signal saturation occurs sooner. This is the scenario plotted in the solid curve of Fig. 7(a). Figure 7(b) illustrates saturation of the experimental data of Fig. 6. Model from Fig. 7(a) is used to fit the data. Remember the fraction round-trip losses of this empty cavity were 7×10^{-5}. One solution to this problem is to increase the input power as the intracavity absorption level rises. A faster chopping cycle could also be used. But in any case this affects only the signal size scale; the recorded decay information is unaffected.

Further improvement of the system includes the use of faster chopping cycles and the replacement of the APD with a sensitive, positive-intrinsic-negative diode in a resonant matching circuit. At present the chopping frequency is limited by the locking loop between the laser and the cavity. After all, the sideband locking system also uses the heterodyne principle, in this case the beat is between the field of the direct reflection off the cavity input mirror and the field leaked out from the cavity storage. If the mode is being switched too fast, the cavity field does not have sufficient time to establish itself as the frequency/phase reference for the incident instantaneous laser field to compare against. The lock will then be based on equal contributions from two weaker cavity fields. Experimentally, there is a transient associated with the switching, and this leads to some problems with the lock's robustness. An alternative is to stabilize the laser on the cavity with a third mode, completely off from the molecular resonance and independent of the other two modes. The third mode can be left on all time to maintain lock while the switching can go on as before between the first two modes. The heterodyne detection rf system can conveniently filter out the contribution from the third mode. The only penalty in this arrangement is a somewhat increased level of shot noise, resulting from the added contribution of the third mode to the photocurrent. A hybrid of the on-resonance/off-resonance switch with transmission heterodyne detection against the third mode is another clear avenue for high-sensitivity detection.

V. Weak absorption measured by field-phase (frequency-domain)

In Section IV the advantages of an enhancement cavity were discussed in a time-domain application. The signal exiting the cavity can also be measured using phase sensitive detection methods, *i.e.* in frequency-domain applications. The phase of the light, along with the cavity resonance structure, is perturbed by the molecular radiation, which leads to additional phase shifts. The objective of this section is to discuss phase-sensitive optical-heterodyne spectroscopy, using an enhancement-cavity, as a tool for signal acquisition. The advantage of this approach lies in the characteristic property of FM spectroscopy: the simultaneous and continuous observation and subtraction of the signal and background optical phases.

As one considers how to probe an external cavity signal with the FM technique, the first approach that comes to mind is to lock the laser frequency to a cavity resonance and then modulate that cavity mode around the desired molecular resonance while monitoring the cavity transmission. This approach is a simple lock-in derivative line shape recovery process. In order for this method to be successful, it is important to have a very tight frequency lock loop between the laser and the cavity because any laser frequency noise relative to the cavity will be converted to amplitude noise. To implement this scheme, a piezoelectric transducer (PZT) is mounted on one of the cavity mirrors. This assembly is used to modulate the cavity length, and the laser tracks the modulation. The modulation frequency is usually limited to the audio range on account of mechanical resonances and roll-off of the PZT and mirror assembly frequency response. Depending upon the laser's amplitude noise spectral distribution, the attainable modulation frequency may be too low to reach shot-noise limited detection. Moreover, the apparent line shape would also be broadened by this modulation process. However, promising results have been obtained. Using a solid-state Nd:YAG laser, locked to a high-finesse (100,000) cavity (corresponding to a ≈1 mHz relative line width), a cavity-dither (at 500 Hz), and lock-in detection a detection sensitivity of 3×10^{-11} (6.4×10^{-13}/ cm) has been measured at 1 s averaging [47].

A. Principle of NICE-OHMS

To benefit from the full noise-reduction advantages of FM spectroscopy, one needs to increase the phase-modulation frequency of the probe field, usually to be much larger than the resonance line width under study. In addition to the laser-cavity locking issue, another obstacle remains; namely, the cavity bandwidth limit. Specifically, FM sidebands at a high frequency are needed to eliminate low-amplitude noise, and at the same time the cavity must respond to the sidebands in exactly the same manner as it responds to the carrier. This will reduce the frequency-to-amplitude noise conversion process. This goal can be realized by frequency modulating the input laser beam at exactly the free-spectral range of the cavity. We then detect and demodulate the cavity-transmitted light at the modulation frequency. Any small residual frequency variations of the laser will still lead to some amplitude fluctuations and phase shifts of the transmitted carrier, but these will also lead to exactly the same amplitude fluctuations and phase shifts of the sidebands, which are transmitted on nearby cavity axial orders. So the transmitted light still accurately represents an FM spectral triplet, with minimal AM conversion caused by the relative laser/cavity frequency jitter. Thus the noise level can approach the intrinsic AM noise level of the laser at the FSR frequency.

Figure 8 shows the case where the central component is used to detect the intracavity molecular resonance, illustrating how the saturated molecular dispersion causes an unbalance of the laser FM spectrum by a phase shift on the carrier component. Initially, all the FM components are lined up on their respective cavity modes. The central cavity mode will then be pulled because of the additional phase shift attributable to the molecular dispersion. After the phase sensitive demodulation, the detector viewing the transmitted light will generate a dispersion signal in the rf beat. We refer to this technique as (laser frequency-) noise-immune, cavity-enhanced, optical-heterodyne molecular spectroscopy (NICE-OHMS) [45, 29, 47, 48]. This modulation and detection scheme makes it possible to use a high-finesse cavity without introducing additional noise.

B. The sensitivity of the NICE-OHMS technique

To estimate the sensitivity associated with NICE-OHMS, we notice that the cavity-enhancement effect applies only to the signal; no additional noise source has been introduced. Therefore the noise-equivalent absorption signal is that of Eq. (7) for ordinary FM spectroscopy, divided by the cavity enhancement factor ($2F/\pi$). The power in the denominator should be that of the cavity transmitted light, P_t.

This argument can be supplemented with a more rigorous proof. Suppose the molecular dispersion changes the intracavity refractive index by Δn, with the shift of cavity resonance given by ($\Delta n \cdot \omega_0$). Light going through the cavity will thus acquire an extra phase shift of $\phi = \arctan\left(\Delta n \cdot \omega_0 / \gamma\right)$, where γ is the cavity HWHM (measured in radians). Following the previous treatment and under the assumption of a small ϕ, we derive

$$\phi \approx \Delta n \cdot \omega_0 / \gamma = \frac{\lambda}{4\pi} \alpha \frac{\omega_0}{\gamma} = \frac{c}{2\gamma} \frac{\alpha d}{d} = \frac{FSR}{\gamma} \cdot (\alpha d) = \frac{2F}{\pi} \left(\frac{\alpha d}{2} \right). \tag{16}$$

The signal amplitude is $\sqrt{2}\eta P_t J_0 J_1 \cdot \phi$ and the shot noise limit is $\sqrt{2eB\eta P_t}$. The minimum detectable absorption at $S/N = 1$ is thus,

$$(\alpha d)_{\min} = \frac{\pi}{2F} \sqrt{\frac{2eB}{\eta P_t}} \frac{\sqrt{2}}{J_0(\beta) J_1(\beta)} \ . \tag{17}$$

When $\beta \approx 1$, this sensitivity result is the same as that expressed in Eq. (15) for the ac chop ring-down method, except for a small numerical factor (≈1.4), an expected result inasmuch as both methods are shot-noise limited. The difference arises from the fact that in the cavity-enhanced frequency modulation spectroscopy, some portion of the carrier power is converted to the sidebands, leading to a slight loss of sensitivity for a fixed total optical power.

A numerical example helps demonstrate the potential of this technique. Suppose the modulation index, β, is 0.5, and the photodiode responsivity, η, is 0.85 A/W. Also, take the optical power, P_t, to be 5 mW and the detection bandwidth, B, to be $1/2\pi$ Hz, which corresponds to a 1 s time constant. Then, for a single-pass cell, the noise-equivalent integrated absorption, $(\alpha d)_{\min}$, is 2.2×10^{-8}. Under the same conditions, a cavity with a finesse of 100,000 improves the sensitivity to 3.5×10^{-13}. As discussed below, a noise-equivalent sensitivity of 5.2×10^{-13} of an integrated absorption at 1 s averaging has been achieved. This corresponds to an absorption of 1×10^{-14}/cm for a cavity length of 50 cm [47].

C. Implementing a NICE-OHMS experiment: signal line shape, size, and sensitivity. An experimental schematic is shown in Figure 9. Two electro-optic phase modulators are used to impose two sets of FM sidebands on the laser beam. Modulation at a low frequency, δ, is detected in the reflected cavity signal and is used to produce an error signal for locking the laser to the cavity. Sidebands at a higher modulation frequency, Δ, are set to the cavity's free-spectral range frequency and are used to probe the intracavity molecular resonances. This signal is detected in transmission, with adequate optical isolation between the cavity and the photodiode. To study the resonance signal line shape and width, a precise scanning capability is important. A frequency-offset locking loop is implemented to permit sweeps with rf resolution of the laser frequency relative to an independent stable reference. During the scan, the cavity FSR changes slightly. To maintain the noise-immune property, the sideband frequency must track this changing FSR.

As shown in Fig. 8, the laser spectrum has three major components: the carrier at ω_L and two phase-modulation sidebands at $\omega_L \pm \Delta$. Each of these three components has its own two sidebands located at $\pm\delta$ away from itself, namely at $\omega_L \pm \delta$, $\omega_L + \Delta \pm \delta$ and $\omega_L - \Delta \pm \delta$, which are not shown in Fig. 8. The three corresponding cavity resonant peaks are denoted as ω_0 and $\omega_0 \pm FSR$, with $FSR = \Delta$. The beam reflected from the cavity carries all these frequency components and is detected by a photoreceiver. Demodulation at frequency δ produces the servo error signal used to lock the laser frequency to the narrow-line width cavity. Because of the additional modulation, this locking error signal now has three contributions. These are the two sideband resonances of strength $J_1(\beta)^2$ near $\omega_0 \pm \Delta$,and the carrier contribution $J_0(\beta)^2$ near ω_0. Together, these additively define the lock point. When none of the laser frequency components is affected by a resonance of the intracavity molecules, the servo error signal keeps the carrier, ω_L, and its two sidebands, $\omega_L \pm \Delta$, on the cavity resonance, ω_0 and $\omega_0 \pm \Delta$. Thus, the transmitted beam has the original, perfectly balanced FM spectra because the carrier (ω_L)and the sidebands ($\omega_L \pm \Delta$) experience the same phase shifts and amplitude attenuations. However, when a molecular resonance affects any of these three components, the interaction converts part of the FM into AM, which is then detected by the photoreceiver viewing the transmitted light.

For example, as shown in Fig. 8, when a molecularresonance is near the cavity resonanceω_0 , the carrier will experience a modified intracavity refractive index, which has been changed by Δn because of the molecular absorption. As a result, ω_0 is shifted by $\omega_m = -\omega_0 \Delta n$. If we neglect for the moment the servo contributions from the two sidebands, then the carrier ω_L could be kept at the new cavity resonance center ($\omega_0 + \omega_m$) and the sidebands, after being shifted to the new positions of $\omega_L \pm \Delta + \omega_m$, will no longer line-up with the cavity resonances. The resulting phase-shifts then lead to the AM signal recovered by the detector viewing the transmitted light. In practice, the two sidebands contribute certain servo error components that will partially offset the servo error signal provided by the carrier. The net result is that the laser frequency will be shifted back by laser servo in the amount of $x = 2\omega_m J_1(\beta)^2$, where x is derived from the requirement that $x J_0(\beta)^2 - 2(\omega_m - x)J_1(\beta)^2 = 0$. Here we have used the approximation that $J_0(\beta)^2 + 2 J_1(\beta)^2 = 1$, valid for the interesting range $\beta \leq 1$. However this shift of locking point causes little effect in the signal detection because it is very small (< 100 Hz) compared with the cavity line width, which is typically a few tens of kHz.

Taking into account the nonlinear molecular phase shift ϕ and the additional phase shift ϕ_x due to the small change in the locking offset, we can express the field of the cavity-transmitted light in the following form,

$$E_t(t) = E_t(0)\left[J_0 \exp[-i(\omega t - \phi_x)] + J_1 \exp[-i((\omega+\Delta)t + \phi - \phi_x)] - J_1 \exp[-i((\omega-\Delta)t + \phi - \phi_x)]\right] \tag{18}$$

We can see that the locking offset phase shift (exp[-iϕ_x]) is a common factor for all three contributions and can be factored out. The signal current at the frequency Δ can be readily derived as

$$i_s \propto J_0(\beta)J_1(\beta)\sin(\phi)\sin(\Delta t) \approx J_0(\beta)J_1(\beta)\,\phi\,\sin(\Delta t). \tag{19}$$

The signal has a pure dispersion line shape and is independent of the laser/cavity locking point. An important aspect of this line shape is that it contains only the odd-symmetric response ~ $\phi\sin(\Delta t)$, and so the line shape and the apparent line center position are independent of any less than optimal setting of the rf detection phase at Δ. This property will allow precise locking to these resonances, even though the rather high modulation frequency generally causes problems in the stability of the detection phase.

We should note that although the requirement of the laser/cavity locking is much more relaxed for NICE-OHMS than in the direct cavity transmission detection, the laser line width still needs to be narrowed so that a stable optical power is effectively coupled into the cavity. For metrology purposes, this laser/cavity locking loop also serves as the short-term frequency stabilizer. For a cavity line width of, say, 10 kHz, it is straightforward to lock a commercially available external-cavity diode laser below 100 Hz relative to the cavity, using a feedback control of the laser diode's current and the PZT of its external grating. Using a solid-state Nd:YAG laser, the combined servo actions of the laser's internal PZTand an external acousto-optic modulator, the laser/cavity relative frequency-noise spectral density was as low as 20 mHz/√Hz. This indicates the laser's line width relative to the cavity is a mere 1.3 mHz. Another important technical issue is that the recovered line shape is influenced by a residual amplitude modulation (RAM) associated and synchronous with FM at the cavity FSR frequency. With an active control loop, RAM at Δ can be eliminated, and the resulting line shape matches the model line shape.

To reject further noise and minimize baseline drift, a small dither can be applied on the cavity resonance (with the modulation amplitude matching the width of molecular resonance) at a low audio frequency. This allows a lock-in detector to process the demodulated rf signal from the output of the double-balanced mixer that is driven at frequency Δ. Hence, the line shape from the rf channel, resulting from modulation detection of an isolated dispersion resonance, approximates the derivative of a dispersion profile [40]. Indeed the experimental data are fit by a theoretical line shape rather well, as shown in Fig. 10, with the fit residual magnified by ten times. Although the intrinsic transition width associated with the (ν_2+3ν_3) P(5) line of C_2HD is on the order of kHz, the observed line width (FWHM) is 705 kHz (after removal of the modulation broadening by the fit) which includes contributions from the power-saturation (≈1.3 times) and pressure-broadenings (≈35 kHz/mTorr) of the 270 kHz transit time line width.

As explained earlier, one way to maintain lock between a laser and cavity, is to dither some component of the system and lock-in on the transmitted light. We refer to this low-frequency operation as DC detection, to differentiate it from the high-frequency rf approach of NICE-OHMS. The line shape measured by using DC detection follows the original Wahlquist formula for a modulation-broadened, derivative line shape [39, 40].

Comparing NICE-OHMS and DC signals, gives us an appreciation for the noise-immune nature of the NICE-OHMS detection, as shown in Fig. 11. This figure shows signals collected using the two techniques and two different laser/cavity lock conditions. Under one set of experiments, the laser and cavity were tightly locked, and in the second, the laser/cavity lock was deliberately set to be loose and even oscillating. We can now compare the recovered signal-to-noise ratios before and after the lock was sabotaged. The DC detection of the intracavity molecular absorption (upper row) is shown to be critically dependent upon the performance of the laser/cavity lock. (A fast laser/cavity frequency-lock servo was used for the graphs obtained in the left column while a slow and noisy servo was used for those in the right column.) However, increased laser frequency noise relative to the cavity yields little effect in FM detection (bottom row).

Figure 12 shows the experimental sensitivity that was achieved using 1.8 mTorr of gaseous C_2HD. The transition under study is the (ν_2+3ν_3) P(5) overtone line of C_2HD. The cavity finesse was 100,000 and the intracavity power ≈300 W, giving a saturation parameter of ≈1.75 and a saturation peak contrast of 13.2%. The single-pass (46.9 cm long cavity) linear absorption was about 3×10^{-8}. Therefore the absolute level of saturated absorption by the intracavity molecules was 4×10^{-9}. This is verified by the DC detection of the cavity transmission, shown in the top graph of the figure. The calibration process involves measurement of the cavity finesse, on-resonance transmission, and reflection dip contrast, from which the residual round-trip cavity losses is calculated. With the laser locked to the cavity with a relative line width of ≈1 mHz, the simple cavity-dither and lock-in detection of the transmission yields a S/N (amplitude/rms noise) of 130 at 1 s averaging. This corresponds to a detection sensitivity of 3×10^{-11} at 1 s. The corresponding S/N from the NICE-OHMS detection is 7700 with a 1 s time constant, as shown in the bottom graph of the figure. This translates into a noise-equivalent detection sensitivity of 5.2×10^{-13} at 1 s averaging, ≈1.5 times worse than the calculated shot-noise limit. The NICE-OHMS result is about sixty times better than the straightforward dither detection, because of its higher modulation frequency and its insensitivity towards the laser frequency noise relative to the cavityAnd we emphasize that the gain in sensitivity by NICE-OHMS over simple dither detection will be even more impressive if we had not done a good job in locking the laser to the cavity.

There is an optimum value of the intracavity sample pressure for the maximum signal size. An increase of pressure raises the size of linear absorption, but at the same time reduces the level of saturation because of the pressure-broadening of the homogeneous transition width. For fixed cavity parameters, change of pressure also influences the input power coupling. Therefore the signal size and its “discriminator” slope vary depending upon the pressure. A useful model of this behavior is based on an axially averaged field picture [49, 50] in which the moving molecules interact with the average standing intra-cavity field. At line center, the counter running waves interact with the same molecules, thus causing the absorption coefficient to be reduced from the off-resonance value of $\alpha_0/\sqrt{1+S}$ to $\alpha_0/\sqrt{1+2S}$. Here α_0 is the linear absorption coefficient at the center of the Doppler profile and S is the saturation parameter. The observed nonlinear signal is thus proportional to

$$\Delta\alpha = \frac{\alpha_0}{\sqrt{1+S}} - \frac{\alpha_0}{\sqrt{1+2S}} . \tag{20}$$

To perform detailed calculations on signal size, we use Eqs. (2) and (3) to determine the cavity transmission, along with the following useful relations: $\Delta n = \frac{\Delta\alpha\lambda}{4\pi}$, $\alpha_0 = \alpha_p \cdot P$, $S = I/I_{sat}$, and $I_{sat} = I_0 \cdot (\Gamma_T + \Gamma_0 \cdot P)^2$. Here Δn is the refractive index change caused by the saturated molecular resonance; α_p is the molecular absorption coefficient per unit length and unit pressure; P is the gas pressure; I_{sat} is the required saturation intensity (W/cm^2); Γ_T is the residual line width, at zero pressure and zero power attributable to transit time broadening; Γ_0 is the pressure broadening coefficient; and I_0 is a power-scaling constant that can be determined experimentally. The natural line width (≈kHz) of a vibrational overtone transition is negligible in a saturation calculation because transit time broadening at room temperature is typically a few hundred kHz. We can calculate in steps, the relative depth of the saturated absorption, the cavity frequency-shift caused by the molecular resonance, and the FM signal size and discrimination slope as functions of gas pressure. With the parameters associated with a typical cavity and gas sample, we find that a pressure around 10 mTorr gives the maximum saturation signal. The model fits to the experimental data rather well, as shown in Fig. 13, which displays the experimental signal slope (signal amplitude/line width) versus pressure. As will be explained later, this slope is used as a frequency discriminator for locking the laser frequency to the molecular transition, so the maximum slope leads to the best locking precision.

The high detection sensitivity of the NICE-OHMS method, opens up many possible spectroscopic applications. For example, some weak transitions have been measured within the tuning range of a Nd:YAG laser at 1.064 μm. Two such lines were measured, $^{12}C_2H_2$ ($2\nu_1 + \nu_2 + \nu_5$) R(12) [51] and $^{12}C^{16}O_2$ ($2\nu_1 + 3\nu_3$) R(6) [52]. These have transition dipole moments of 50 μDebye and 6 μDebye, respectively (1 Debye = 3.33564×10^{-30} C · m). These absorption lines are weaker than the C_2HD ($\nu_2 + 3\nu_3$) P(5) transition, which has a transition dipole moment of ≈70 μDebye [53]. Using the same gas pressure, optical power, and cavity dither amplitude, the saturated absorption signals of CO_2, C_2HD and C_2H_2 are compared in Fig. 14. The C_2H_2 transition is recovered with an excellent signal-to-noise ratio, as shown in Figure 14 (c). The signal size is about 0.23 of that for C_2HD, at the same gas pressure and optical power. It provides another frequency reference for the Nd:YAG laser.

The $^{12}C^{16}O_2$ ($2\nu_1 + 3\nu_3$) R(6) transition shown in Fig. 14 is quite different than either of the acetylene lines. For one thing, the saturated absorption signal is much weaker than the C_2HD line, by more than a factor of 350. More strikingly, the recovered line shape associated with the transition is vastly different. Nevertheless, this spectrum can be fit using two separate resonances that have different line centers and line widths. Interestingly, the narrower negative-going peak indicates a physical process reversed from the normal saturated absorption. The intracavity optical power was 410 W, where the saturation of this CO_2 transition is estimated to be only about 2% in the free-flight regime. As the input power is reduced by a factor of four, the resonance line shape remained relatively unchanged. The signal size, however, decreased roughly by the square of the power change. The line shape did not depend upon the laser dither frequency either. The change of the dither amplitude, on the other hand, had a larger impact on the signal size of the relatively wider peak, causing an apparent change on the signal line shape. But this change is well accounted for by the two resonance model, and the fit was able to produce consistent line widths corresponding to a fixed gas pressure. As the intracavity gas pressure was changed, line width broadenings and line center shifts were observed for both peaks. Extrapolated to zero pressure, the inverted peak has a width of ≈100 kHz.

This CO_2 resonance involves two quanta of symmetric stretch and three quanta of antisymmetric stretch in the C-O bond. The bending mode (ν_2) is not excited. The lifetime of the excited vibrational state is estimated to be ≈2 ms, with relaxation dominated by IR fluorescence through the vibrational transition $(2, 0^0, 3) \rightarrow (2, 0^0, 2)$. The relevant molecular constants are given in Ref. [54]. One likely explanation for the abnormal (sign-reversed) part of the line shape in the CO_2 spectrum is that it arises from a near-resonant two-photon absorption transition in the neighborhood of the one-photon resonance, which we see as a *saturated* absorption resonance. This idea is supported by the fact that the zero-pressure line width of the inverted peak, only about 100 kHz, is just half of that dictated by the transit time broadening (210 kHz). It is as if during the transit, the molecule experiences twice as many radians of signal phase, for example by resonating with a two-photon response. Alternatively, there may be a quantum interference resulting from the state mixing of the excited vibrational state.

D. A NICE-OHMS application: Laser Frequency Stabilization

The NICE-OHMS technique can provide us with the line centers for weak molecular lines in the visible wavelength region with metrological precision. The narrow line widths associated with saturated line shapes are especially useful, as the line centers are narrowly defined, which improves the long-term stability of a light source locked to such a transition. Moreover, the high signal-to-noise ratio improves short-term stability, permitting more effective intercomparisons among various frequency standards. With the narrower line width—but lower S/N—of the C_2HD overtone transition, a frequency stability comparable to that of the I_2 -stablized system has already been achieved [55, 56].

The NICE-OHMS spectrometer provides laser frequency discrimination information relative to both the cavity resonance and the molecular transition. It is thus an ideal system with which to achieve simultaneously good short- and long-term frequency stabilizations. As discussed earlier, the laser tracks the cavity resonance to within a few mHz. The vibrational noise and long-term drift in the cavity can be suppressed by stabilizing the cavity to an intracavity molecular resonance. The NICE-OHMS signal is intrinsically dispersive when the molecular resonance is probed by the carrier of the FM triplet. Used for locking, this could basically eliminate the influence of the local oscillator frequency drift on the recovered line center. In practice it is necessary also to dither the cavity length and make a second-harmonic signal recovery of the rf mixer output. This is partly to suppress the baseline offset problem associated with the imperfect FM modulation at the FSR frequency. Figure 15 shows such a discrimination curve associated with the C_2HD transition. Another important issue concerns the final line shape under the conditions of FM with a residual AM part (RAM) [57, 58]. The effect of RAM is to add an even-symmetric absorption-phase component to the originally pure dispersion line shape. Unfortunately, this line shape alteration caused by RAM cannot be corrected by the cavity-dither process. To achieve the best stabilization results, it is crucial that the FM has a zero (or at least a small constant) residual AM. .

To demonstrate that NICE-OHMS is useful for generating frequency-stabilized light, an overtone-stabilized Nd:YAG laser at 1.064 μm was beat against a frequency-doubled Nd:YAG/I_2 reference system [55]. (The 532 nm-stabilized laser has a stability $\approx 5\times 10^{-14}$ at 1 s, as determined from beating experiments with two I_2-stabilized systems.) Figure 16 shows the counted beat frequency versus time. The drift is ≈5 Hz/h and a 60 Hz frequency noise at 1-s counter gate time, in agreement with the S/N available from the C_2HD resonance at 1.064 μm. The doubled light from the reference Nd:YAG laser is locked on I_2: R(56) 32-0, component a_{10}. The mean value of the beat frequency between the two lasers was measured to be at 5252.2261 ± 0.0026 MHz, which determines the absolute frequency of the P(5) line in the $(\nu_2 + 3\,\nu_3)$ band of $^{12}C_2HD$ to be 281,635,363.979 MHz ± 3 kHz. In a similar experiment, the center frequency of the $^{12}C_2H_2$ $(2\nu_1 + \nu_2 + \nu_5)$ R(12) line was determined to be 281,612,403.295 (.014) MHz, i.e., it is 17708.458 (.014) MHz red of the iodine-locked reference laser.

One representation of the frequency stability is the Allan variance [59]. The Allan variance is calculated by comparing adjacent frequency measurements and then averaging over the whole data set. The time interval between the adjacent measurements is the averaging time for the frequency noise. The Allan variance permits one to separate and isolate different noise processes based on their time scales. Rather than the variance, it is customary to plot its square-root, called the Allan deviation. In the short-time domain, the Allan deviation typically displays a slope of $1/\sqrt{\tau}$, where τ is the averaging time. This is because the main contribution to the fast noise originates from white frequency noise, for example, shot noise. One sees from this argument that the level of this short-term deviation is controlled by the ratio between the frequency discrimination line width and its S/N. Figure 16 also shows the Allan deviation determined from the beat record of the two stabilized lasers. The frequency deviation is normalized to the optical carrier frequency, i.e., 282 THz (1.064 μm). The Allan deviation of $\sigma_y = 2\times10^{-13}/\sqrt{\tau}$ improves to 6×10^{-15} at a longer integration time (>1000 seconds), a promising indicator for an ultrastable frequency reference. This frequency stability, achieved by locking to an extremely weak reference transition, is a direct result of the spectrometer's high detection sensitivity. Notice that the C_2HD-stabilized system shows only three times more frequency noise than the I_2 system, which is notable because the I_2 transition strength is almost a million times stronger than the P(5) line of the C_2HD ($\nu_2 + 3\ \nu_3$) overtone band. The short-term frequency stability of the optical sources can be comparable to or better than the state-of-the-art microwave standards. However, the reproducibility and accuracy of optical frequency measurements are not yet comparable to microwave standards.

One approach to reducing some of the systematic shifts of the reference frequency is to slow down the motion of the target quantum absorber, thereby reducing the second order Doppler effect. Slower speeds also imply longer interaction times. Slower molecules give a narrower line width because the natural life-time of vibrational transitions usually far exceeds (more than 300 times, for the acetylenes) the transit-controlled interaction time, limited by the laser field dimensions. While effective schemes for molecular cooling and trapping are emerging, optical selection of slow molecules based on interaction time has been actively pursued since the late 1980s [60-62]. The idea is this: the homogeneous line width originating from collisional broadening can be reduced by lowering the gas pressure until the mean-free-path of molecules becomes much larger than the transverse field dimension. This is referred to as the transit-time regime. To optically select the slow molecules, a low optical power is necessary so that the low Rabi frequency leads to appreciable saturation only for the slowest molecules. The observed signal is thus dominated by interaction with the slowest molecules and consequently the effective interaction time is increased, limited finally by saturation and residual pressure broadening. Unfortunately, this avenue toward line width reduction is expensive in *S/N*, scaling approximately according to the fifth power of the instrumental resolution increase.

In the free-flight regime, molecules with the mean thermal velocity cross the laser beam without suffering any collision. In other words, if we define the collision-broadened homogeneous line width (the half-width at half maximum) as Γ_p and the transit-time line width as Γ_T, then $\Gamma_p << \Gamma_T$, with $\Gamma_T = (\pi/4) <V_\perp>/w_0$, where w_0 is the laser beam-waist radius and $<V_\perp>$ is the mean transverse velocity. A second important time scale is the inverse of the collisional line width Γ_p. The slowest molecules are those with transit times longer than $1/\Gamma_p$. These molecules spend their whole life-time inside the field, though they are still in a collisional regime. These molecules have a constant and velocity-independent saturation parameter *S*, controlled primarily by the collisional broadening,

$$S = \frac{\mu^2 E^2}{\hbar^2 \Gamma_p^2}, \tag{21}$$

where μ is the transition dipole moment and E is the optical field amplitude. Faster molecules with transit time shorter than $1/\Gamma_\mathrm{p}$ are in a free-flight regime and their saturation parameter depends on their transverse velocity. Defining τ as the interaction time ($\approx 4w_0/V_\perp$) then S equals unity when $(\mu E/\hbar)\tau = \pi$. The optical power required to saturate molecules with transverse velocity $V_\perp$ is thus

$$Power_{(S=1)} = \left(\frac{c\varepsilon_0}{2} E^2\right)\pi w_0^2 \Big/ 2 = \frac{c\varepsilon_0}{2}\left(\frac{\pi\hbar}{\mu}\frac{V_\perp}{4w_0}\right)^2 \frac{\pi w_0^2}{2} = \frac{\pi^3}{64}\frac{\hbar^2 c\varepsilon_0}{\mu^2} V_\perp^2 \,. \tag{22}$$

Interestingly, the saturation power is independent of the mode size in the transit-limited regime. However, the necessary saturation power does increase as the square of the transverse velocity, and it can be vastly different for slow and average thermal molecules because it as been assumed that $\Gamma_\mathrm{p} << \Gamma_\mathrm{T}$. In short, a sufficiently low gas pressure can be used to create a free-flight regime, and a low power beam then optically selects for the slow molecules. The selection is based on the saturation effect. The resulting signal line width becomes strongly inhomogeneous, with molecules from different transverse velocity groups contributing different intensities and widths. Slow molecules will dominate the contribution to the signal amplitude, and the width is essentially the homogeneous line width Γ_p. Faster moving molecules will see a reduced saturation and will mostly contribute to the wings of the resonance. The width is caused by transit effects and increases with velocity.

This concept has been demonstrated using NICE-OHMS. In the experiment, a <2 mTorr sample gas was used, and the mean-free-path of molecules is then ≈30 times longer than the transverse field dimension. The cavity input power was reduced by a factor of 75 from normal operation. Figure 17 shows a resonance line width of ≈20 kHz, without correction for the modulation broadening by a 30 kHz peak-to-peak dither of the cavity. This is thirteen times narrower than that set by the room temperature transit-time-limit and is mainly limited by the relatively high pressure (1.8 mTorr). The selected molecules have a temperature of ≈1.8 K. The signal-to-noise ratio is vastly reduced, as the optical power is smaller than usual and the majority of molecules do not contribute to the observed saturation signal. In fact, compared with the number of molecules participating in the normal saturation spectroscopy, the slow molecule selection process has reduced that number to only a fraction of 0.75%. At present the limited S/N associated with the low power has prevented us from taking full advantage of this narrow line width. With an improved system this approach will enable us to access the information of free molecules with minimized second order Doppler shift, thereby creating an optical frequency standard of potentially high accuracy.

VI. Concluding remarks on signal extraction and cavity enhancement

Dramatic progress has been achieved in optical detection sensitivity by joining molecular spectroscopy with resonator physics. The methods discussed in this chapter emphasized the importance of separating the molecular signal from the cavity's stored field, and the advantage of detecting signals where only fundamental physical processes introduce noise. We noted the importance of determining the cavity's response simultaneously for the on-resonance and off-resonance cases, so these quantities can be subtracted from the measured signal to reveal the molecular absorption of interest. We have discussed how the FM method of NICE-OHMS can be used to implement this signal isolation and subtraction in real time. A repetitive transient heterodyne detection scheme, with lowered technical requirements on the laser system, that meets these design principles was also discussed. While these methods are likely to find many applications, there are other simpler techniques, discussed elsewhere in this book, that offer practical capabilities in applications where shot-noise limited detection sensitivity is not necessarily required.

One exciting application of the spectroscopic method discussed in the chapter is high-resolution, vibration overtone spectroscopy. Coupling this method with large, intracavity beam modes and slow moving molecules [63-65], we expect hyperfine structures and recoil splittings will be measured in overtone transitions in the near future. The precision with which these transitions can be measured should also make it possible to realize a comb-like series of frequency references from the near infrared region into the visible. This goal can be achieved with new light sources [66, 67, 68], and the systematic study of overtone spectra. In short, the sensitive spectroscopic methods presented in this chapter should allow for the construction of detailed pictures of molecular structure and dynamics and accurate optical frequency and wavelength reference networks.

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Figure Captions

Fig. 1 (a) An intuitive picture of atomic absorption: μ is the atomic dipole moment, λ the transition wavelength, γ the spontaneous decay rate, g_0 the coherent coupling between the atomic dipole and the light field quantized within the volume of $(a \cdot d)$, and σ_0 represents the resonant atomic absorption cross-section. (b) Notation for the fields in and out of an optical cavity. The standing-wave field built-up inside the cavity is shown, along with the radiation field from the prepared atomic dipole.

Fig. 2 Principle of optical (homodyne) heterodyne detection of an absorption signal.

Fig. 3 Experimental set-up for chopped heterodyne ring-down spectroscopy. The two AOMs provide the necessary frequency offset between the two modes and are chopped out-of-phase. The laser is locked to cavity. The heterodyne beat between the two modes at the cavity transmission is demodulated against the known carrier frequency to produce the decay signal. PD: photodiode; APD: avalanche photodiode; PBS: polarized beam splitter.

Fig. 4 Comparison of the demodulated ring-down curve between the empty cavity (right column) and the cavity with additional absorption (left column). The chopping period $\Delta t = 4\tau_{cav}$, and the time axes are normalized to τ_{cav}. Shown from top to bottom are the switching dynamics of mode 1, mode 2, their product (beat), and the difference signal between the neighboring half cycles.

Fig. 5 A representative trace of the chopped ring-down curve of the empty cavity, obtained from the video output of the rf spectrum analyzer. A theoretical fit and the fit residual are also shown.

Fig. 6 Demodulated heterodyne beat amplitudes between the two chopped cavity modes (left column) in the presence of intracavity absorption (labeled in the graph). Shown in the right column is the absorption signal obtained by differencing the beat amplitudes in the adjacent half cycles.

Fig. 7 (a) Signal contrast vs. intracavity molecular absorption. The change of cavity input coupling efficiency is (not) taken into account in the solid (dotted) curve. (b) Experimental data from Fig. 4, showing signal saturation when the molecular absorption approaches the empty cavity loss (35×10^{-6} single pass).

Fig. 8 The optical spectrum and the detection principle for NICE-OHMS: ω_L denotes the laser frequency and Δ is the phase-modulation frequency that matches the cavity *FSR*. The original FM symmetry is upset when the molecular dispersion shifts a cavity resonance by ω_m.

Fig. 9 General schematic of the NICE-OHMS spectrometer, showing the major components of the laser/cavity locking, the transmitted sideband detection, and the precision tuning control.

Fig. 10 Frequency scan of the C_2HD ($\nu_2+3\nu_3$) P(5) transition line shape and overlaid theoretical fit, with fit residuals magnified by ten times.

Fig. 11 Demonstration of the noise-immune property of NICE-OHMS. The C_2HD ($\nu_2 + 3\nu_3$) P(5) resonance signal is recovered by both cavity-dither lock-in (DC) detection and NICE-OHMS technique, under the conditions of a tight laser/cavity lock (left column) and a poor lock (right column).

Fig. 12 Sensitivity measurement of the NICE-OHMS technique. The upper graph shows the level of the saturated absorption while the lower graph shows the corresponding *S/N* obtained via NICE-OHMS. The noise equivalent detection sensitivities (normalized to 1s time constant) are 3×10^{-11} for cavity dither detection and 5.2×10^{-13} for NICE-OHMS.

Fig. 13 Signal slope recovered from the NICE-OHMS spectrometer with respect to the pressure of the intracavity gas sample.

Fig. 14 Line shape comparison among the resonances of (a) CO_2, (b) C_2HD, and (c) C_2H_2, under the same experimental conditions.

Fig. 15 Molecular discrimination signal used for stabilizing Nd:YAG laser, obtained by the second derivative recovery of the dispersion signal detected by NICE-OHMS.

Fig. 16 Stability of beat between I_2-stabilized and C_2HD-stabilized Nd:YAG lasers. Allan deviation is determined from the beat record. The frequency noise of the beat is still limited by the C_2HD system, which is about three times worse than the I_2 system.

Fig. 17 With low power and gas pressure, optical selection of slow molecules produces a line width thirteen times below the room-temperature transit-time-limit.

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